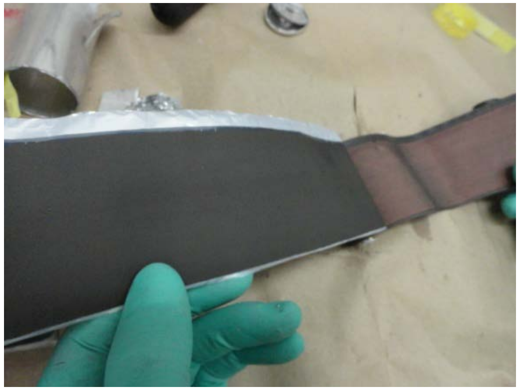
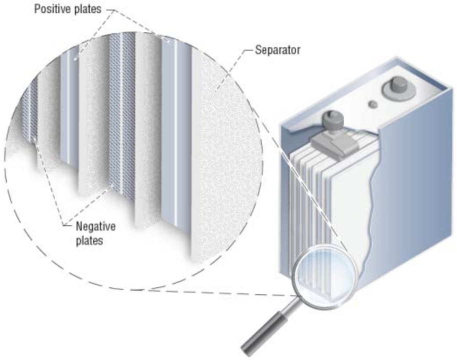
A Summary on Progress in Materials Development for Advanced Lithium-ion Cells for NASA's Exploration Missions





Concha M. Reid, NASA Glenn Research Center

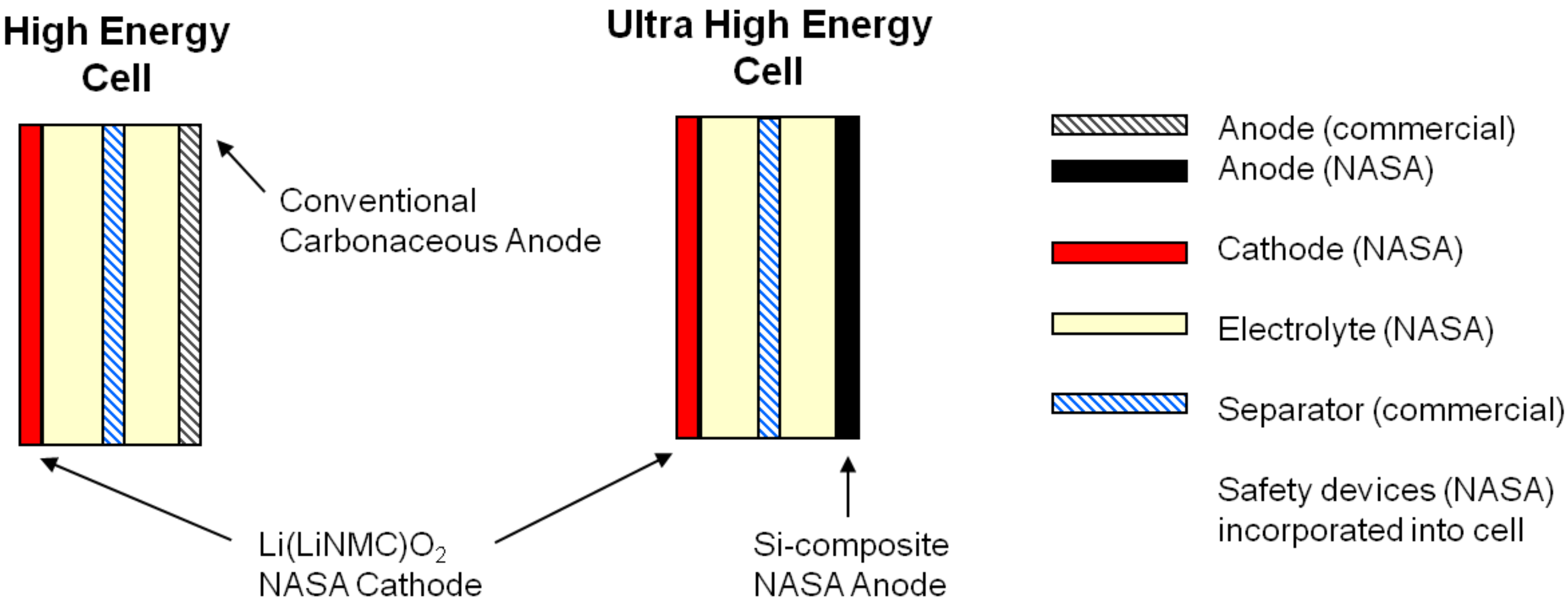
2011 NASA Aerospace Battery Workshop
Huntsville, AL
November 15-17, 2011

Objectives

- NASA is developing advanced Li-ion cells to enable or enhance future human missions to Near Earth Objects, such as asteroids, planets, moons, libration points, and orbiting structures.
- Advanced, high-performing materials are required to provide component-level performance that offer the required gains at the integrated cell level.
- This paper discusses results after two years of development and efforts that are continuing into a third year that offer the promise of delivering high performing, mature materials.

*Specific details on many of the technical efforts discussed in the paper can be found in the papers from the focused session :"Advanced Materials and Cell Components for NASA's Exploration Missions", NASA Aerospace Battery Workshop, Huntsville, AL, Nov. 2009.

Advanced Li-ion Cell Development



High Energy Cell

- Lithiated mixed metal-oxide cathode $Li(LiNMC)O_2$/ Graphite anode
- **180** Wh/kg (100% DOD) @ cell-level, 0^0 C and C/10
- 80% capacity retention at ~**2000** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)

Ultra High Energy Cell

- Lithiated mixed metal-oxide cathode ($Li(LiNMC)O_2$)/ Silicon composite anode
- **260** Wh/kg (100% DOD) @ cell-level, 0^0 C and C/10
- 80% capacity retention at ~**200** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)

Preliminary system requirements given in: Reid, Concha, M., Miller, Thomas B., Manzo, Michelle A., and Mercer, Carolyn M., “Advanced Li-ion Cell Development for NASA’s Constellation Missions”, NASA Aerospace Battery Workshop, Huntsville, AL, Nov. 2008.

Development Goals Were Addressed Through a Combination of Contracted Efforts (NRA, SBIR) and NASA In-house Efforts

ANODES
- Georgia Tech Research Corporation (GTRC)
- Lockheed Martin Space Systems Company (LMSSC)
- NASA GRC

CATHODES
- University of Texas at Austin (UTA)
- NEI Corporation
- NASA JPL

SAFETY
- Physical Sciences, Inc.
- Giner Corporation

ELECTROLYTES
- Yardney Technical Products
- NASA JPL

Summary of Two Years of NRA Contract Cathode Development

On Target:

- In Year One, very low first cycle reversible capacity was measured on all cathode deliverables (50-70% of charge capacity was delivered on the first discharge).
  - ✓ First cycle reversible capacity has improved and on some materials is now better than that of typical Li-ion cathodes.

- First year manufacturability studies revealed that Tap Density, a critical metric for raw powders, was too low to fabricate practical cathodes. Development efforts were directed to improve tap density in their second year.
  - ✓ Tap Density has improved to better than the minimum value necessary by using alternate synthesis methods (1.5 g/cc minimum).

- Specific capacity declined as a result of change in cathode synthesis methods to improve tap density.
  - ✓ Optimizations were performed to maximize specific energy while maintaining tap density at or above minimum levels necessary for manufacturability.

Still need improvement (current values not yet at or approaching goals):

- ➢ Specific Capacity, both at room temperature and at lower temperatures
- ➢ Temperature performance (percentage of room temperature capacity retained at 0° C)
- ➢ Discharge rate capability
- ➢ Cycle life
- ➢ Combination of attributes that meet or exceed goals in one material

Summary of NRA Cathode Results

Metric	Goal	Best Values*		Values for Latest Materials	
		Value	Material	UTA 23 mo. coated	NEI 23 mo. uncoated (interim)
First Cycle Reversible Capacity (%)	81	87	UTA 18 & 23 mo. coated	87	65
Specific Capacity ,RT, C/10 to 3V (mAh/g)	311**	238	UTA 11 mo. uncoated	164	191
Specific Capacity, 0° C, C/10 to 3V (mAh/g)	280	135	UTA 11 mo. coated	126	130
RT Capacity Retention at 0° C (%)	90	72	NEI 23 mo. uncoated (interim)	85	72
Tap Density (g/cc)	$\geq$ 1.5	> 2.3	NEI and UTA, both 18 mo. uncoated	2.02	1.34
Rate Capability at C/5 as compared to C/10 (%)	95	83	NEI 6 mo. uncoated***	***	***
HE Cycle Life (cycles)	2000	81	UTA****	****	****
UHE Cycle Life (cycles)	250	81	UTA****	****	****

Notes:
* Best Values are the highest value of that particular metric achieved from the development. Values are not necessarily for the same material.
** Expected minimum value based on desire to attain at least 10% of RT capacity when performing at 0° C.
*** Rate capability studies not performed routinely on all samples.
**** Cycle life studies not routinely performed. Number of cycles to 80% of initial capacity was projected from 60 cycles of data collected at the vendor on experimental materials (not necessarily provided as a deliverable).

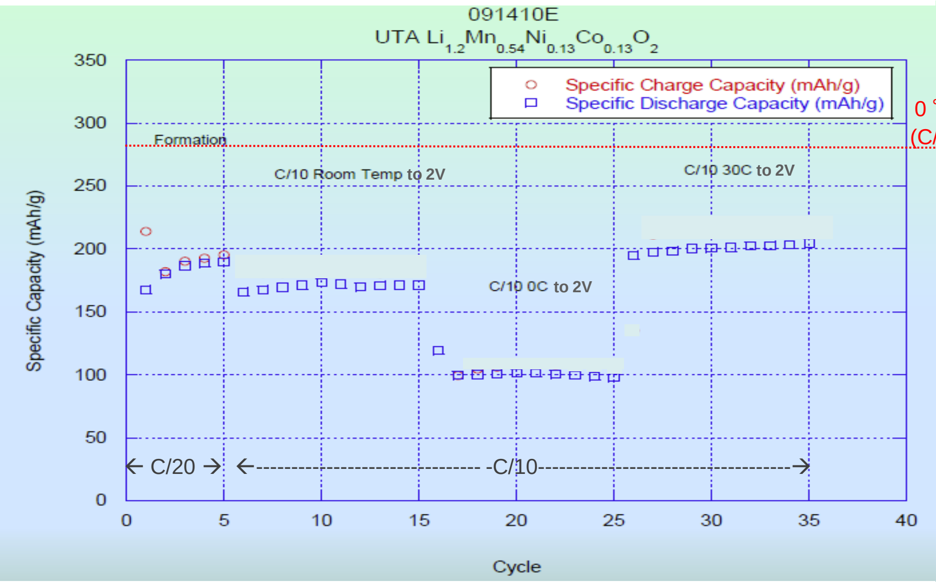
Performance of University of Texas at Austin (UTA) NMC Cathodes

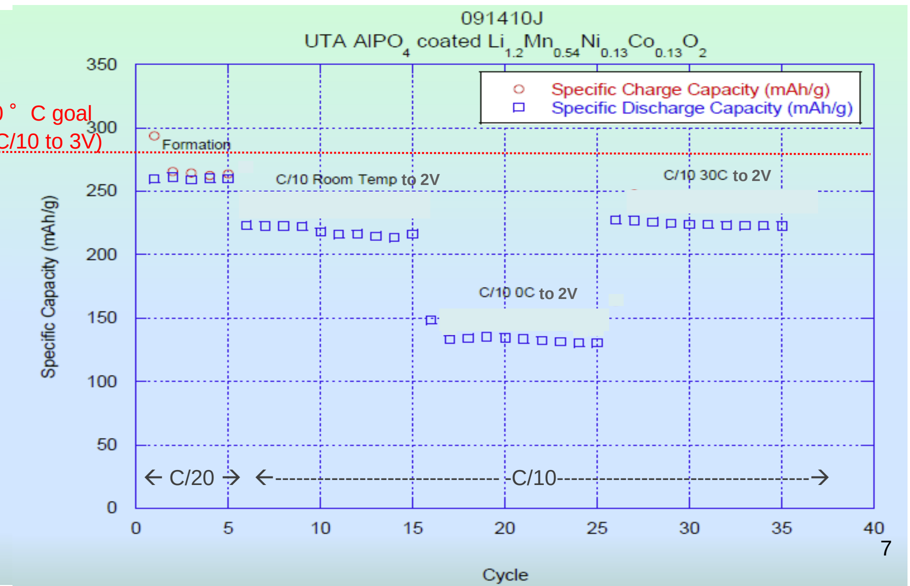
Accomplishments:

- Improvements in specific capacity,1st cycle reversible capacity and temperature performance
- Tap density exceeds goals required for manufacturability
- Successful use of alternative cathode synthesis procedures and application of coatings to improve tap density and material performance
- Coated materials exhibit improved performance over uncoated
- Several conference papers and publications

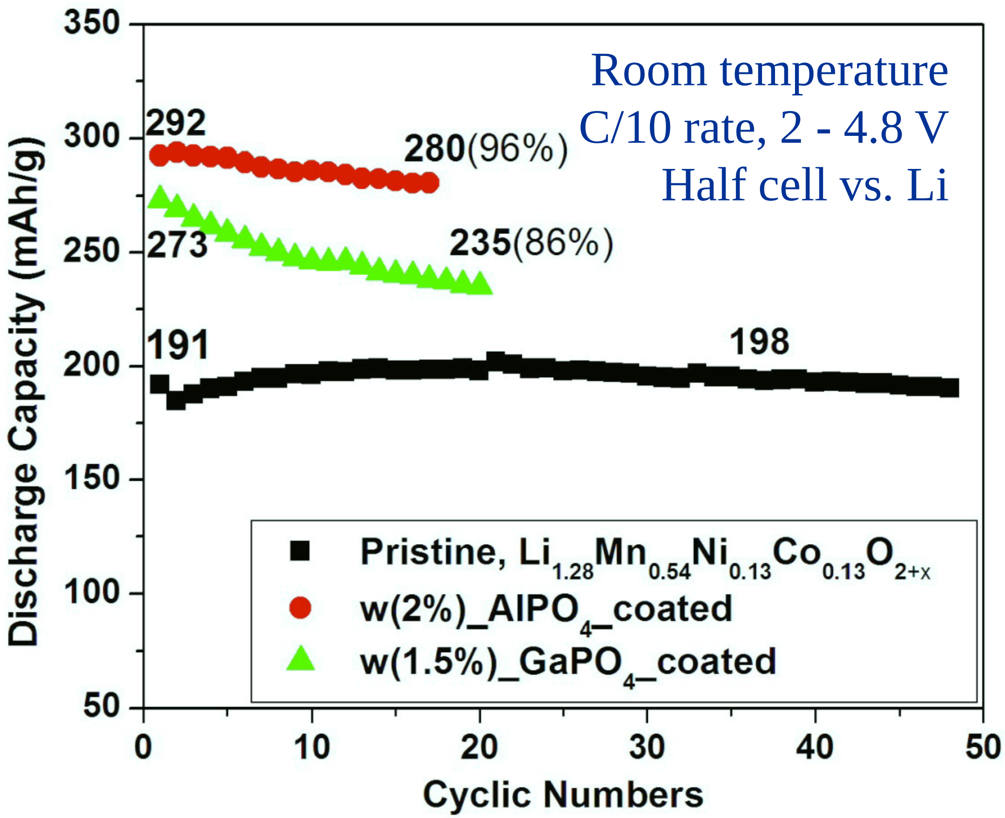
Remaining Challenges to meet goals:

- Higher specific capacity at RT and low temperatures
- Better temperature performance (higher percentage of RT capacity retained at low temperatures)
- Improved rate capability
- Demonstrated cycle life
- Combination of attributes that meet or exceed goals in one material





University of Texas at Austin Cathode Development Follow-on Effort
Preliminary Results



Surface modification of the optimized sample demonstrates an initial specific capacity of 292 mAh/g and high tap density (>1.8 g/cm^3).

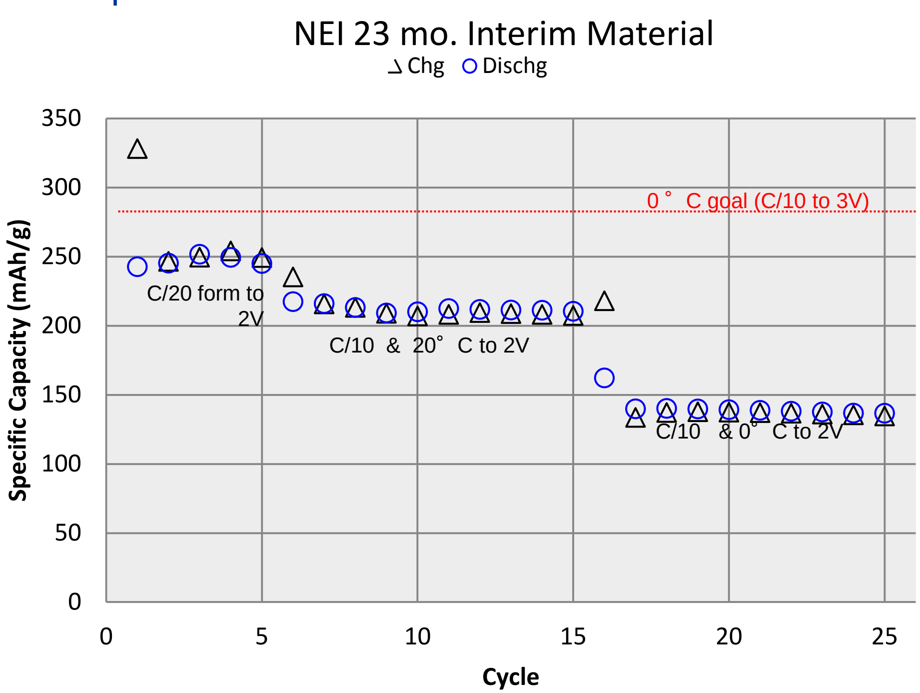
Performance of NEI Corporation (NEI) NMC Cathodes

Accomplishments:

- Improvements in specific capacity,1st cycle reversible capacity, temperature performance, and tap density
- Use of alternative annealing environments to improve tap density
- Performed studies of relationship between tap density, tape density, and surface area to improve loading and optimize materials for manufacturability
- Several conference papers and publications

Remaining Challenges to meet goals:

- Higher specific capacity at RT and low temperatures
- Higher tap density on higher capacity materials
- Higher 1st cycle reversible capacity
- Better temperature performance (higher percentage of RT capacity retained at low temperatures)
- Improved rate capability
- Demonstrated cycle life
- Combination of attributes that meet or exceed goals in one material



Summary of Two Years of NRA Contract Si-composite Anode Development

On Target:

- Specific capacity at C/10 and 0° C has exceeded goal value, outperforming SOA carbonaceous anodes by >3X (>1200 mAh/g vs. ~372 mAh/g).
- Excellent capacity retention has been achieved at 0° C, and has a tendency to improve with cycling in some materials.
- Rate capability at C/2 has exceeded that of SOA carbonaceous anodes (as % of C/10 capacity retained at C/2 rate and RT).
    - 93% for MPG-111 and >94-100% in Si:C anodes.

Still need improvement (current values not yet at or approaching goals/metrics of SOA materials):

- Reversible capacity
- Loading
- Coulombic efficiency
- Demonstration of cycle life in cells

Summary of NRA Anode Results

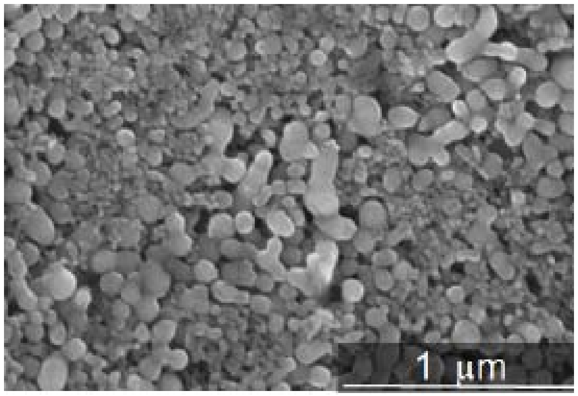
Metric	Goal	Best Values*		Values for Latest Materials	
		Value	Material	GTRC 23 mo.	LMSSC 23 mo.
Total Reversible Capacity (after 2-3 cycles) (%)	89	70	GTRC 23 mo.	70	4
Specific Capacity ,RT, C/10 (mAh/g)	1110	1660	LMSSC 6 mo.	1598	1209
Specific Capacity, 0°C, C/10 (mAh/g)	1000	1528	GTRC 23 mo.	1528	1186
RT Capacity Retention at 0°C (%)	90	107**	GTRC 18 mo.	96	98
Loading (mAh/cm^2)	3.7	3.0	GTRC 11 mo.	0.9	2.7
Rate Capability at C/2 as compared to C/10 (%)	93	103**	GTRC 18 mo.	94	81
Coulombic Efficiency (%)	99.5	98.8	GTRC 23 mo.	98.8	97.9
Projected Cycle Life (cycles to 80% of initial capacity)	250	Virtually no fade after 45 cycles at C/2 at RT**	GTRC 23 mo.	Virtually no fade after 45 cycles at C/2 at RT**	~23***

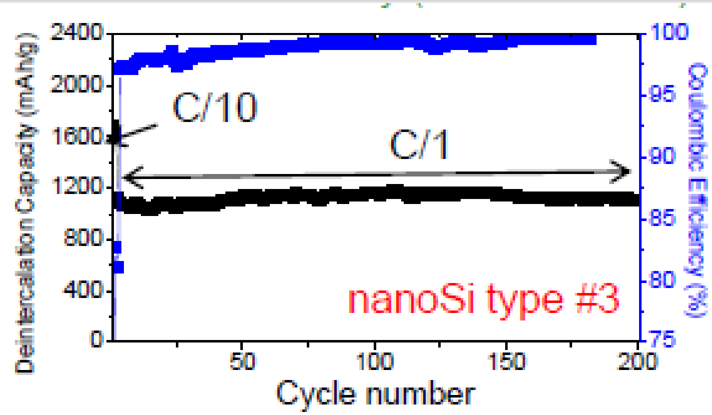
Notes:
*Best Values are the highest value of that particular metric achieved from the development. Values are not necessarily for the same material.
**Capacity improved with cycling.
***Issue of significant capacity fade observed in half-cell testing. Issue of high irreversible capacity and low operational/useable capacity implies difficulty in meeting cell-level specific energy goals.

Ultra High Energy Lithium-ion Battery Anode Development

Georgia Institute of Technology (GT) and Georgia Tech Research Corporation (GTRC)
in partnership with Clemson University

<u>Anode Material</u>:
Nano-silicon-carbon composite with binder





Achieved >1100 mAh/g capacity at a C/1 rate for 200 cycles with GT materials. Data was collected at GT.

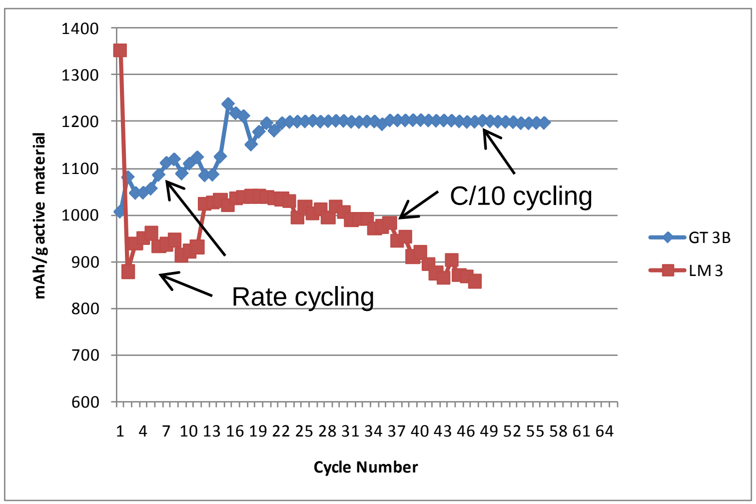
<u>Fundamental Studies Addressed</u>:

- Binder properties & modifications
- Electrolyte additives
- Silicon-binder interfacial properties
- Silicon SEI properties
- Cell “conditioning” effects
- Theoretical modeling

<u>Technical Issues</u>:

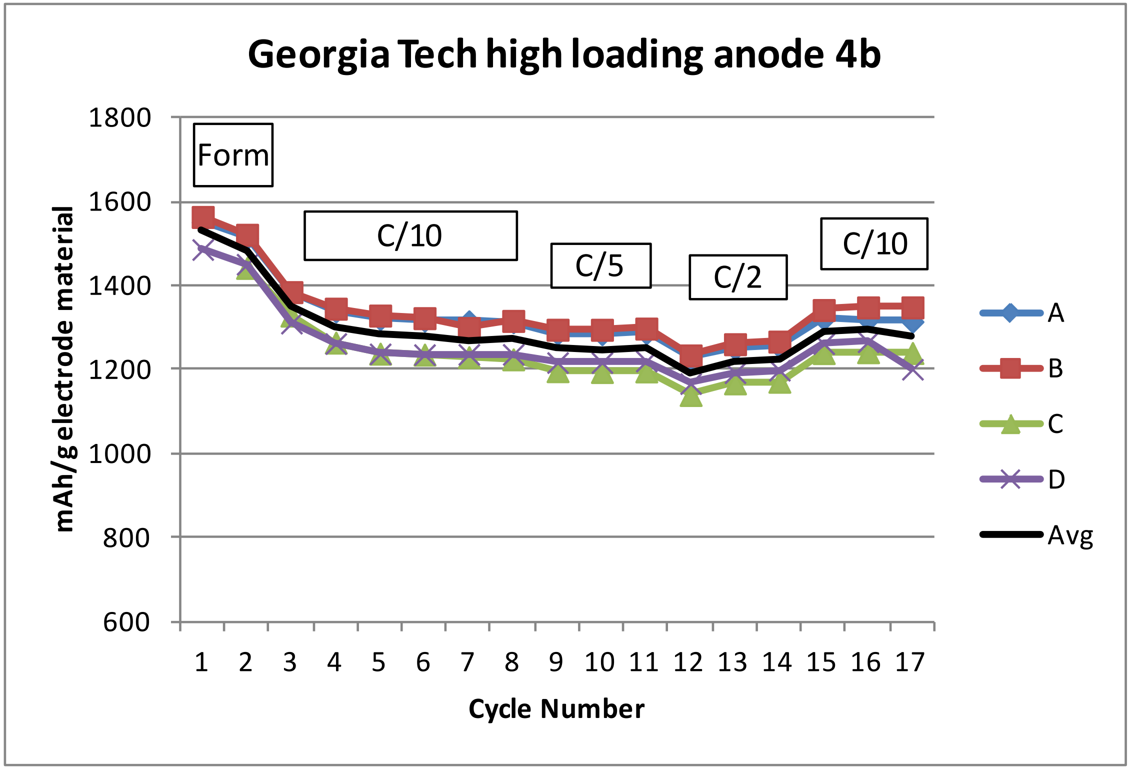
- SEI stabilization to reduce capacity fade
    - Optimal cell “conditioning” parameters
- Low electrode loading
- Stabilization of silicon volume changes
- Optimal electrolyte composition, salts & additives to achieve long-term cycling ability

Technical approaches to address these issues have been proposed



Half-cell cycling performance of a GT anode (blue) compared to Lockheed Martin Space Systems Company (LMSSC) anode material (red) [stable capacity retention on GT materials achieved with the addition of VC (vinylene carbonate) to the electrolyte, no impact on LMSSC materials]

Georgia Tech Anode Development Follow-on Effort
Preliminary Results

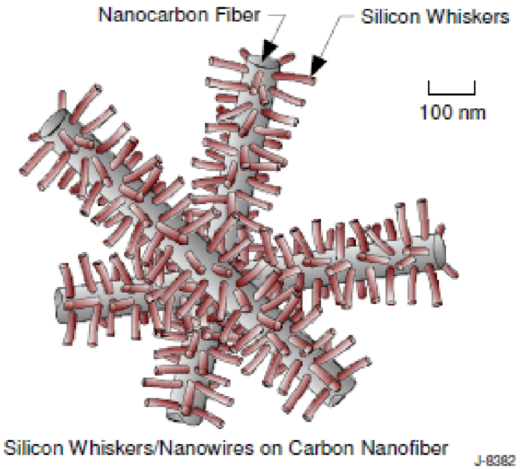


Total electrode material mass loading of 2.2 – 2.6 mg/cm^2 (based upon loading needed to match NMC cathode in a full cell)

- **High-loading anodes demonstrated better specific capacity than the low-loading anodes during the initial cycles (>1300 mAh/g at C/10 at both 20º C & 0º C), but demonstrated significant capacity fade with continued cycling**
- **High-loading anodes cycled at C/2 & 20º C at GRC showed capacity fade to ~600 mAh/g after ~75 cycles, whereas the low-loading anodes demonstrated superior cycle-life performance with continued high capacity (> 80% retention at >250 cycles & 23º C)**

Physical Sciences, Inc. NASA SBIR Overview

PSI Concept: Formation of a Silicon Whisker and Carbon Nanofiber Composite



Silicon Whiskers/Nanowires on Carbon Nanofiber

Material Advantages:

- High in free volume;
- Free of polycrystalline domains (not achievable for silicon anode by CVD);
- Tailorable silicon loadings;
- Supporting matrix forms an electronically conductive framework;
- Processable using established procedure and equipment.

C. Lang, et. al., Electrochemical Performance of Silicon Whisker and Carbon Nanofiber Composite Anode, 220th ECS Meeting, Boston, MA, October 2011

- **Key SBIR Program Accomplishments:**

- **Material synthesis scale-up to 50 gram batches achieved in Phase II with path identified for ~ 500 gm batch synthesis**
- **Demonstrated equivalent coin and pouch cell performance**
- **Developed a technique to reduce the composite agglomeration**
- **Demonstrated 1000 mAh/g performance at up to C/2 rate in full cells**
- **Demonstrated improved cycling performance with VC addition in full cells**
- **Casting procedure scaled-up to produce higher electrode loadings (> 3 mAh/cm^2)**
- **Developed a setup and plan to produce ~20 feet electrode casts**

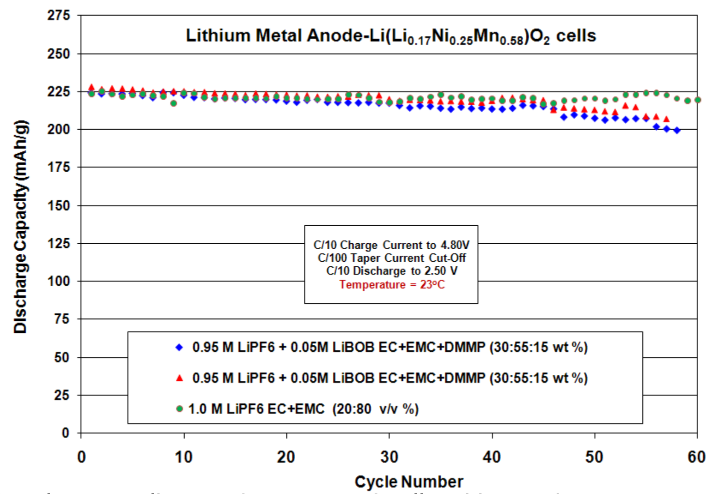
Electrolytes

- Goal: Develop flame-retardant and/or non-flammable electrolytes that are stable up to 5V.

Technology Challenges	Current approaches to address
Electrolyte that is stable up to 5V.	Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes.
Non-flammable or flame retardant electrolyte.	Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance.
High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system).	Combine flame retardant additives with electrolyte formulations with high voltage stability. Operate systems to high voltages and investigate impacts on rate capability, specific energy, energy density and life.
Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and compatibility (wettability).	Develop electrolytes that are not excessively viscous to ensure that the ionic conductivity is sufficiently high over the desired temperature range and the separator wettability is adequate.

Electrolytes

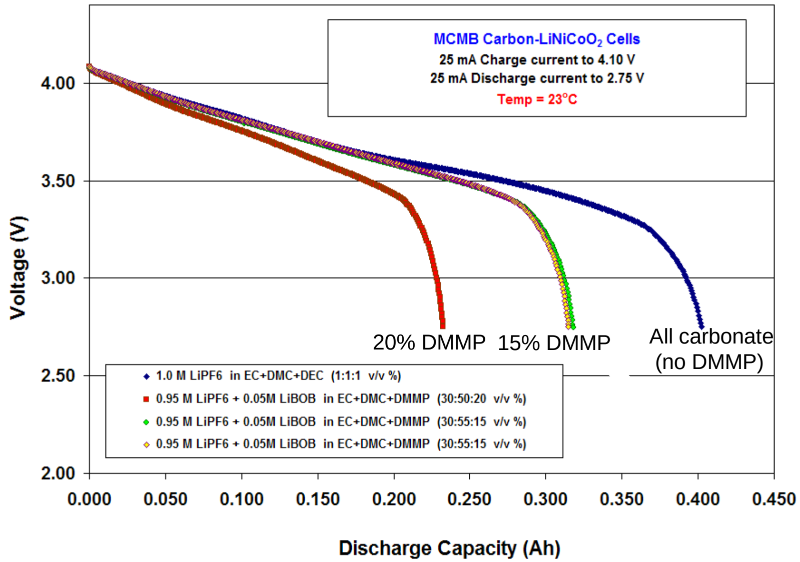
Yardney Technical Products (YTP) in partnership with the University of Rhode Island (URI)



High voltage cycling performance of cells with YTP/URI DMMP-containing electrolytes as compared to an all carbonate-based formulation.

Description	Electrolyte	Percentage Flame Retardant Additive	SET/s	Standard Deviation
"Baseline" Electrolyte	1.0M $LiPF_6$ in EC/EMC (3:7)	None	33.4	3.4
JPL GEN #1 Electrolyte	1.0M $LiPF_6$ in EC/EMC/TPP (2:7.5:0.5) + 2% VC	5% TPP	22.45	2.3
JPL Electrolyte	1.0M $LiPF_6$ in EC/EMC/TPP (2:7:1) + 2% VC	10% TPP	9.57	0.9
JPL Electrolyte	Salt and carbonate blend	15%TPP	3.78	1.2
Yardney/URI GEN #2 Electrolyte	1.0M (95% $LiPF_6$ + 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	15% DMMP	1.8	1.5
Yardney/URI GEN #1 Electrolyte	1.0M (95% $LiPF_6$ + 5% LiBOB) in EC/EMC/DMMP (3/5/2)	20% DMMP	0.4	0.4

Self-Extinguishing Times of Developmental Electrolytes. Data was generated by the University of Rhode Island.



Discharge capacity of MCMB-$LiNiCoO_2$ cells with YTP/URI DMMP-containing electrolytes as compared to an all carbonate-based formulation

- Flame-retardant electrolytes containing dimethyl methyl phosphonate (DMMP) display excellent self extinguishing properties and good stability at high voltages (4.8V), but exhibit poor capacity in cells containing graphite.

Electrolytes

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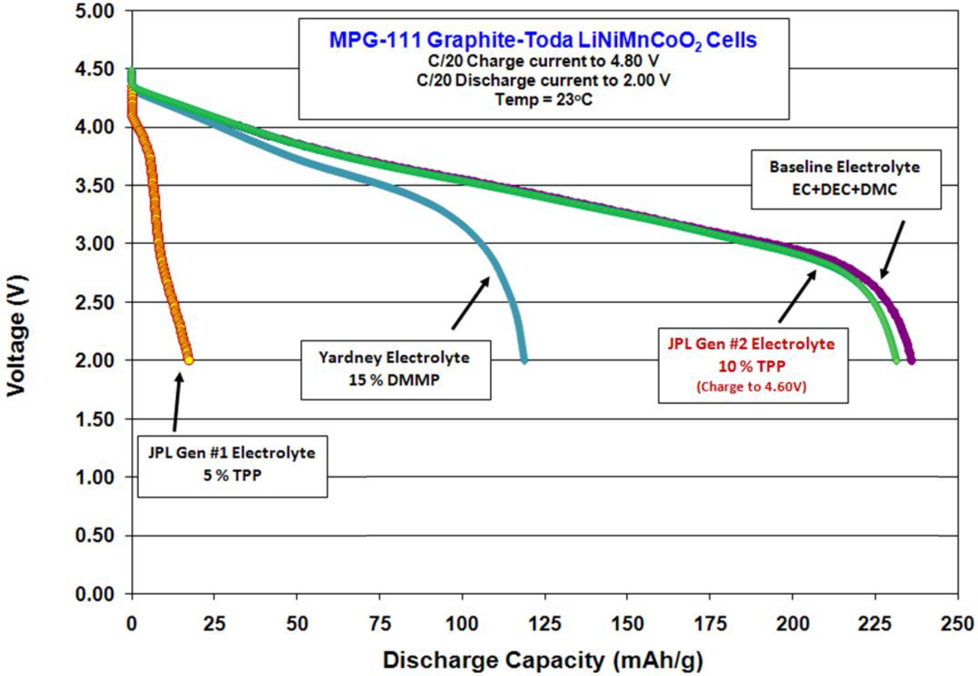
Self-Extinguishing Times of Developmental Electrolytes. Data was generated by the University of Rhode Island.

- Flame-retardant electrolytes containing triphenyl phosphate (TPP) display good self extinguishing properties and stability at high voltages (4.8V), and exhibit excellent capacity retention and cycling stability in cells containing graphite



Discharge capacity of graphite-$Li(LiNMC)O_2$ cells at high voltage with NASA JPL TPP-containing electrolytes as compared to an all carbonate-based formulation

Next steps:

- Optimization of flame-retardant electrolytes that are compatible with Si
- Incorporate electrolyte advancements into production cells

Summary of Safety Component Development with Physical Sciences, Inc. (PSI)

Objective:

•Coat metal oxide cathode powders with lithium cobalt phosphate coatings to improve thermal stability.

Accomplishments:

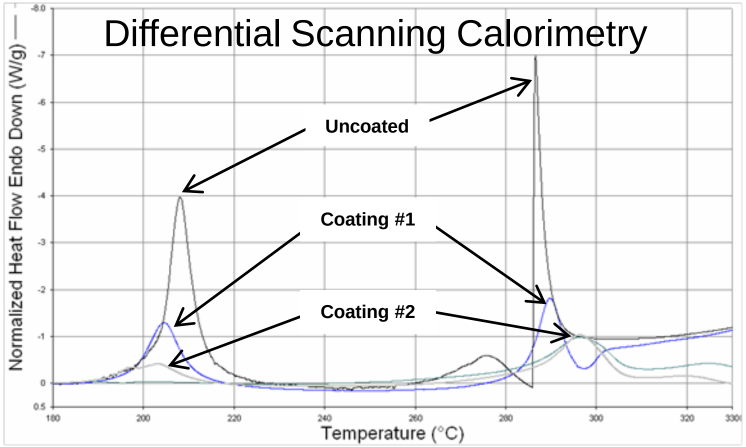
- Demonstrated robust adhesion of coating on $LiCoO_2$ cathodes in half cells for 200 cycles, cycling at C-rate with capacity retention of ~90% of 1st cycle capacity.
- Developed coating and processes to coat NMC cathode materials.
- Coated TODA 9100 NMC cathodes demonstrated <1% loss in discharge capacity over 50 cycles at a C/5 rate.
- Demonstrated to reduce exotherms without reducing performance on high voltage cathodes (Toda 9100 NMC).
- Higher capacity, higher tap density lower irreversible capacity, and better cycling stability demonstrated on coated Toda 9100 NMC cathodes as compared to uncoated cathodes.

Next steps:

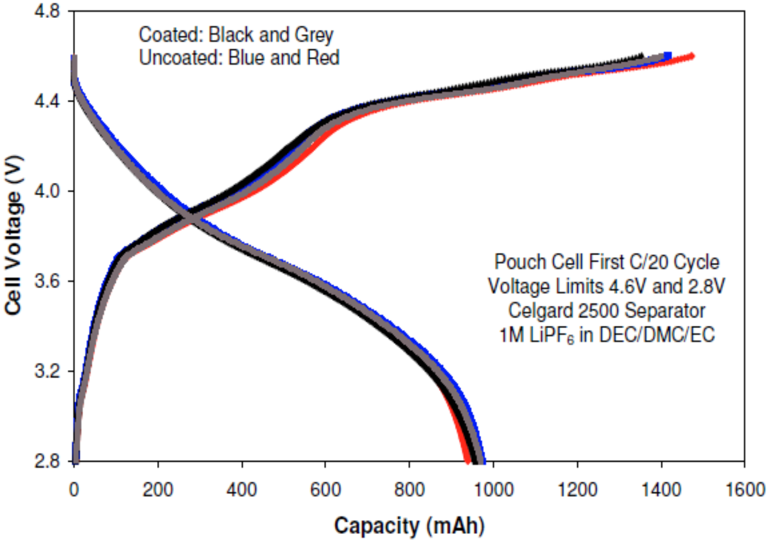
•Physical Sciences, Inc.
  - •Coat NEI 23 mo. deliverable with coating and process developed for Toda NMC materials.

•Under separate effort (most likely with Saft)
  - •Produce electrodes from PSI-coated NEI cathodes.
  - •Build cells containing PSI-coated NEI cathodes.

•NASA independent assessments:
  - •Determine impact on safety and abuse in full cells.
  - •Demonstrate cycling, rate, and low temperature performance.



Preliminary results show reduced heat flow in exotherms of coated Toda 9100 NMC cathode. Data was collected at PSI.



Cells containing uncoated and coated TODA 9100 NMC (2 cells of each) display similar first cycle capacity. Data was collected at PSI.

NASA In-house Component Development and Fundamental Efforts

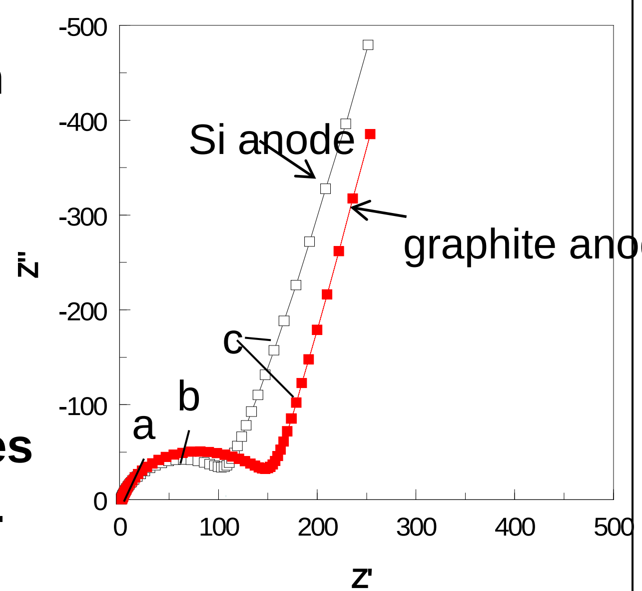
In-house NASA efforts continue to address select components and technical issues necessary to continue to advance technology

- **Anode fundamental studies**
- **Cathode development**
- **Electrolyte Development**
- **Cell Integration**

NASA in-house anode fundamental studies (GRC)

- **Optimization of anode formation and cycling procedures**
- **SEI layer formation**
- **Understanding of electrolyte impact, and additives**
- **EIS (impedance) and cyclic voltammetry studies**
- **Analytical studies - morphology, changes with cycling**

A



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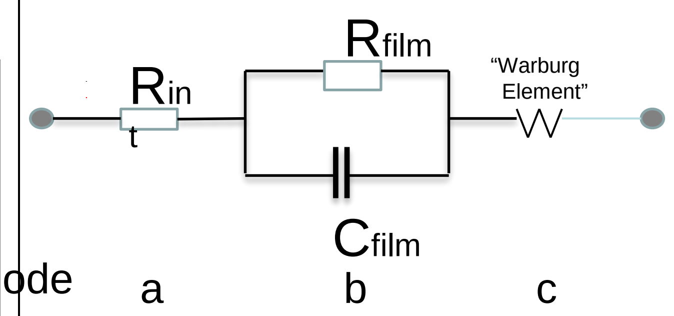
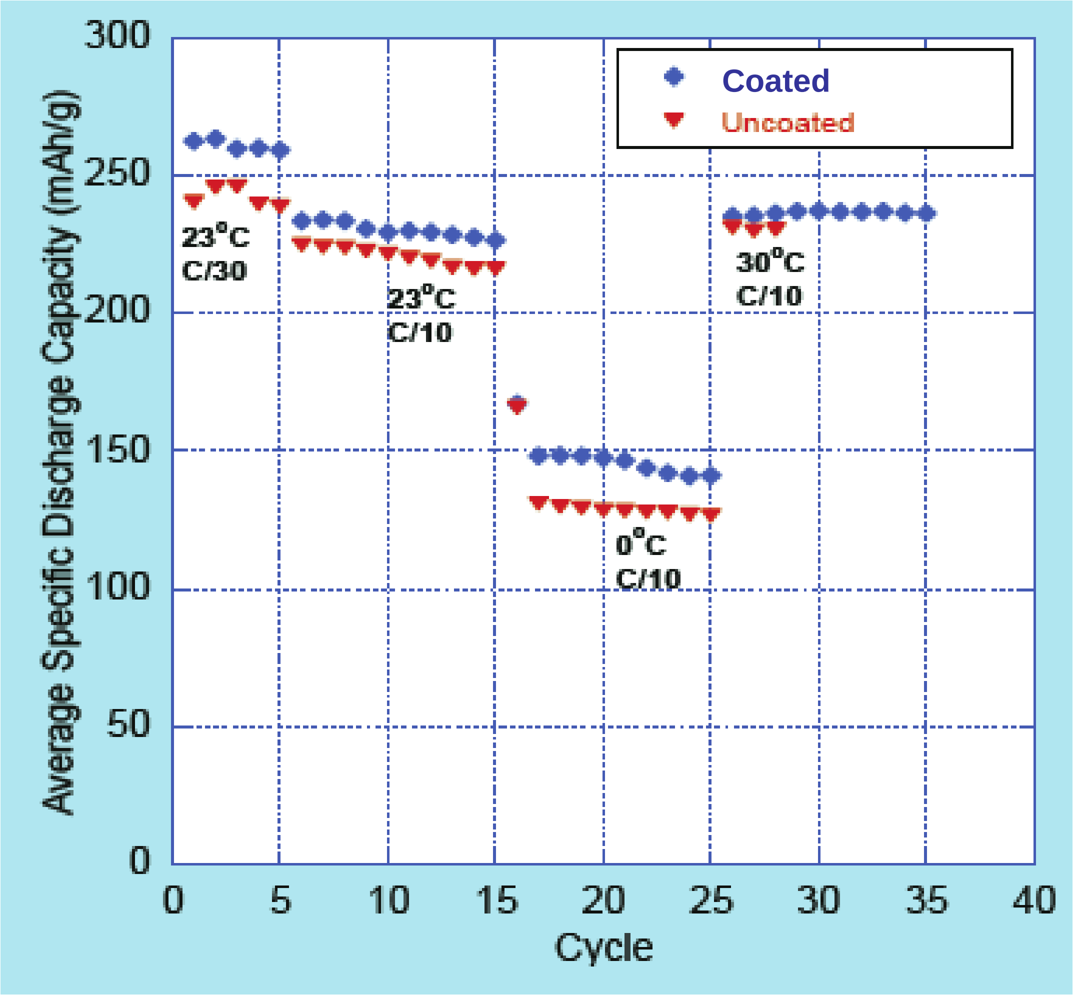


Fitting data / Anode type	Rint (Ω)	Rct (Ω)	Cdl (F)
Si-anode	1.62	94.12	6.34×10^{-6}
C-anode	1.43	125.44	5.02×10^{-6}

NASA In-house Cathode Development (JPL)

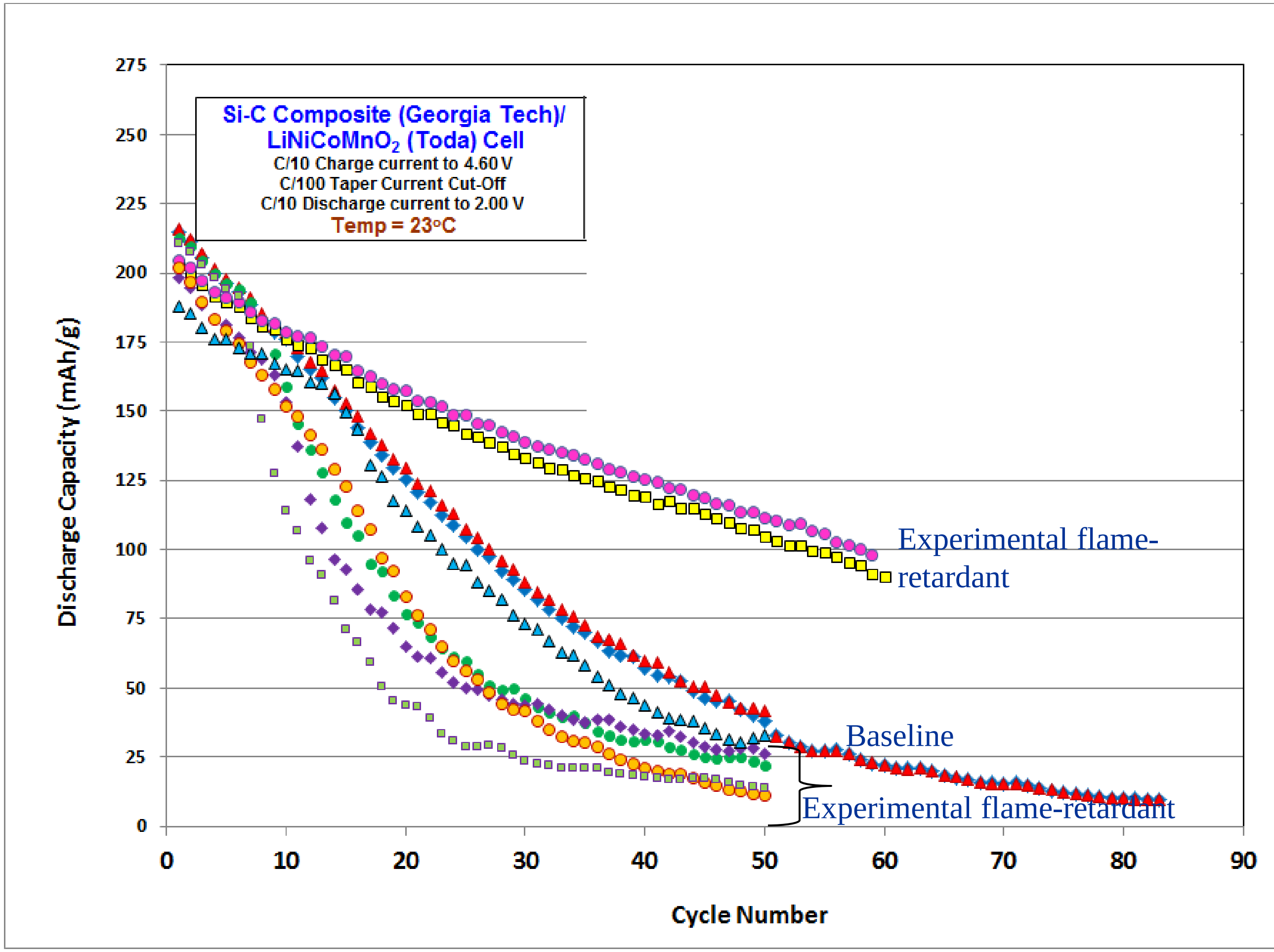
Employing mechanical methods to improve performance

- Ball milling and annealing improved tap density (2.0 g/cm^3)
- Surface modification improved specific capacity over uncoated samples
- Coated samples demonstrated less 1st cycle irreversible capacity loss than similar NMC materials (24 mAh/g)



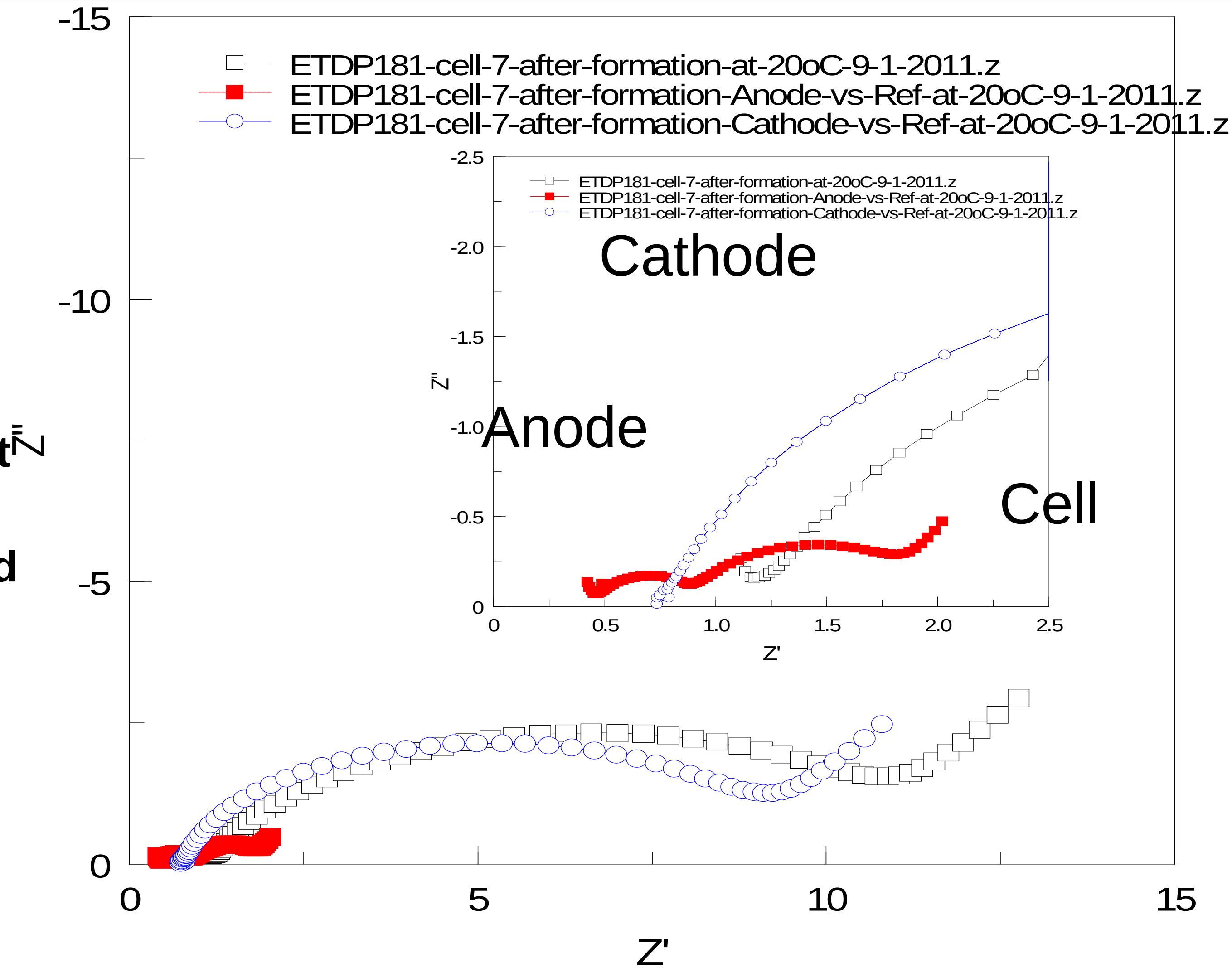
NASA In-house Electrolyte Development (JPL)

- **Developing high voltage flame retardant electrolytes that are compatible with graphite/NMC and Si-based/NMC systems.**
- **Preliminary results show improved performance with some flame-retardant blends over baseline, however capacity fade is much greater in Si-based/ NMC cells (cathode-limited) than in Si-based/Li half cells.**



Cell Integration (GRC)

- **Understanding of electrolyte impact, additives, and quantities**
- **Optimization of cell cycling protocols**
- **Study of component compatibility**
- **EIS (impedance) and cyclic voltammetry studies**
- **Cell modeling and projections**



Electrochemical impedance spectroscopy (EIS) of cell containing Si-based anode and NMC cathode (w/reference)

Next steps in Developing NASA’s Advanced UHE Li-ion Cells

- Component development efforts will culminate in the delivery of components for test, verification, and integration studies at NASA and Saft America
- VL3A-design cells (nominal 6.5 Ah with standard components) are scheduled to be built with components that have reached maturity
  - Cells containing JPL flame-retardant electrolyte, commercial NMC cathode and graphite anode currently in production at Saft America
- Next sets of cells scheduled to be built March 2012
  - Will contain Georgia Tech Si-based anode, UTA NMC cathode, and JPL flame-retardant electrolyte
- Cells will be tested at NASA for electrical performance, safety and abuse

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